

## In Memory of Davide Calamari (Section Editor: Paola Gramatica)

## Benzotriazoles, Alkylphenols and Bisphenol A in Municipal Wastewaters and in the Glatt River, Switzerland

Dimitra Voutsas<sup>1,2</sup>, Paul Hartmann<sup>1</sup>, Christian Schaffner<sup>1</sup> and Walter Giger<sup>1\*</sup><sup>1</sup> Swiss Federal Institute of Aquatic Science and Technology (Eawag), 8600 Dübendorf, Switzerland<sup>2</sup> Environmental Pollution Control Laboratory, Department of Chemistry, Aristotle University, 54124 Thessaloniki, Greece

\* Corresponding author (giger@eawag.ch)

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## Abstract

**Background.** Many organic micropollutants occur at trace concentrations in municipal wastewater effluents and in the aquatic environment. Some of these xenobiotic chemicals can be considered as 'emerging' contaminants and some are suspect to have endocrine disrupting effects. Among the latter are nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA), which deserve special attention due to their ubiquitous occurrence in the aquatic environment.

The complexing agents benzotriazole (BT) and tolyltriazole (TT) are applied as anticorrosive agents (e.g. in cooling and hydraulic fluids, in antifreezing fluids, in aircraft deicing fluids, in dish washing liquids for silver protection), as antifogging agents and as intermediates for the synthesis of various chemicals. The environmental occurrence of NP and OP is caused by the fact that they are intermediate products (metabolites) in the biodegradation of alkylphenol polyethoxylate surfactants. BPA is globally used for the production of polycarbonate and epoxy resins.

**Methods.** BT, TT, NP, OP and BPA were quantitatively determined in municipal wastewater effluents in Switzerland and in the Glatt River. The analytes were enriched by solid-phase enrichment. BT and TT were determined underivatized by electrospray LC/tandem MS. Reversed-phase LC was performed on octylsilica columns with isocratic water/methanol elution. Multiple reaction monitoring of the positive ions provided selective and sensitive detection for reliable quantifications. NP, OP and BPA were determined by GC/MS after derivatization with N-methyl-N-(trimethylsilyl)-trifluoroacetamide.

**Results and Discussion.** BT and TT concentrations in primary and secondary effluents of municipal wastewater treatment plants varied from below 10 to 100 µg/L. The ranges of the concentrations in the Glatt River in ng/L were 636–3,690 for BT, 122–628 for TT, 68–326 for NP, 6–22 for OP and 9–76 for BPA. The corresponding mass flows in g/d were 93–1,870 for BT, 18–360 for TT, 24–183 for NP, 1–16 for OP and 2–72 for BPA. The concentrations and mass flows of NP in the River Glatt were drastically lower than the analogous values found 15 years ago. Thus, a substantially decreased environmental exposure can be observed due to the reduction of the use of alkylphenol polyethoxylate surfactants in Switzerland. The current concentrations of NP, OP and BPA are within the ranges reported for weakly impacted surface waters.

**Conclusion.** The investigated contaminants occur at quantitatively measurable but varying concentrations in municipal wastewaters and in the Glatt River reflecting their ubiquitous input into wastewaters and their different behaviour during biological wastewater treatment.

**Keywords:** Alkylphenol; benzotriazole; bisphenol A; corrosion inhibitors; endocrine disrupters; nonylphenol; octylphenol; tolyltriazole; xenoestrogens

## Introduction

The complexing agents benzotriazole (BT) and tolyltriazole (TT, a mixture of 4- and 5-methyl isomers in benzene ring of BT) (Fig. 1) are widely used as anticorrosive agents (e.g. in cooling and hydraulic fluids, in antifreezing fluids, in aircraft deicing fluids, in dish washing liquids for silver protection etc), as chemical intermediates for dyes, pharmaceutical, fungicides, as antifogging constituents in photographic applications and as ultraviolet stabilizers (Hart et al. 2004). These compounds are characterized by high water solubility (28 and 7 g/L, respectively), low vapor pressure and low octanol water distribution coefficients (log  $K_{ow}$ : 1.23 and 1.89, respectively) (Hem et al. 2003, Hart et al. 2004).

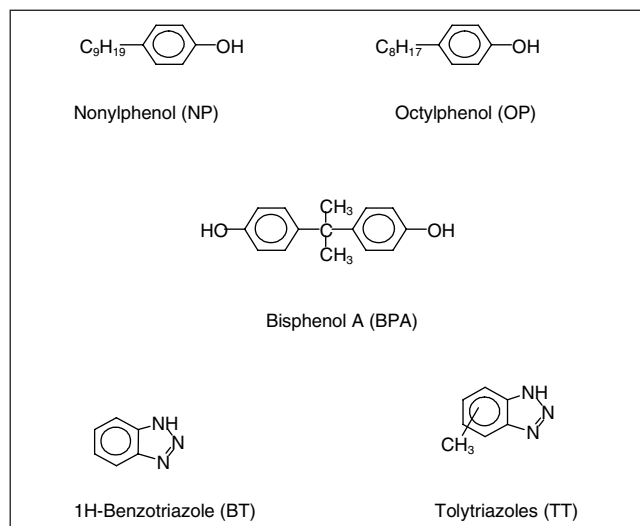


Fig. 1: Chemical structures of the investigated analytes

Moreover, these compounds are quite persistent to biodegradation. Consequently, it must be expected that they occur in wastewaters and eventually in ambient waters. The EC<sub>50</sub> (15 min) concentration for Microtox R (*Vibrio fischeri*) was 4.25 mg/L. A chronic 21 d reproduction toxicity test using *Daphnia magna* resulted in a NOEC value of 3 mg/L. Benzotriazole is classified as toxic to aquatic organisms that can cause long-term adversary effects in the aquatic environment (Cancilla et al. 1998, Cancilla et al. 2003, Hem et al. 2003).

Many studies have revealed the widespread occurrence of low level concentrations of organic micropollutants, (alkylphenol polyethoxylates, pharmaceuticals, natural and synthetic hormones, phthalates, brominated compounds, etc) and their metabolites in the aquatic environment (Montgomery and Reinhard 2003, McArdell et al. 2003, Boyd et al. 2004, Suzuki et al. 2004). These chemicals are often considered as 'emerging contaminants'. Some of these compounds are suspect to have endocrine disrupting properties in particular showing estrogenic activity. Nonylphenol (NP), octylphenol (OP) and bisphenol A (BPA) are important xenoestrogens and deserve special attention due to their ubiquitous occurrence in the aquatic environment.

The environmental occurrence of NP and OP is mainly caused by their appearance as intermediate products (metabolites) in the biodegradation of alkylphenol polyethoxylate surfactants. BPA is globally used for the production of polycarbonate and epoxy resins. NP and OP are used for manufacturing the nonionic surfactants alkylphenol polyethoxylates (APnEO). APnEO are among the most widely used surfactant classes, non ionic surfactants, which have been in use since 1940s. In Western Europe the consumption of APnEO is approximately 92,000 t/y. These compounds are used in domestic and industrial applications as detergents, emulsifiers, wetting agents, dispersants or solubilizers. Among APnEO, nonylphenol polyethoxylates are by far the most commonly used, encompassing about 80% of the world market, whereas octylphenol polyethoxylates account for 15–20% (Knepper and Berna 2003). Several studies confirm the presence of short chain metabolites (APnEO, APnEC, CAPnEC, n=1–2) and nonethoxylated phenolic compounds NP and OP in raw sewage influents, final effluents and in receiving waters (Ahel et al. 1994a, Bennie et al. 1997, Isobe et al. 2001, Spengler et al. 2001, Montgomery-Brown et al. 2003, Gross et al. 2004, Johnson et al. 2005). The short chain ethoxylated or nonethoxylated degradation intermediates are more toxic and exhibit higher endocrine activity than the parent compounds. NP are identified as priority hazardous substances under the EU Directive 2000/60/EC, whereas OP are currently subject to review for inclusion in this category. The potential adverse effects of these compounds to humans and microorganisms resulted in the reduction of the use of alkylphenol polyethoxylates in several countries either through voluntary replacement or by legal regulations. In Switzerland, nonylphenol ethoxylates have been banned from laundry detergents since 1987. However, almost 400 t/y of these compounds are still used for industrial purposes.

BPA (Fig. 1) is used as a raw material for the production of many polycarbonate and epoxy resins that accounts for almost 96% of the production, worldwide. Other applications include its use as a stabilizing agent in plastics, as an antioxidant in tire production, as basic chemical for the production of the common flame retardant tetrabromobisphenol A and as additive in thermal papers or paper coatings. The annual consumption of BPA in the EU is estimated at approximately 680,000 t. Due to the widespread application of BPA, it is commonly found in air, raw sewage effluents, industrial wastewaters and in receiving surface waters (Fürhacker et al. 2000, Spengler et al. 2001).

**Table 1** gives an overview on the reported concentrations of NP, OP and BPA in rivers of 14 countries. The maximum NP concentrations were found in the Glatt River in Switzerland before Switzerland banned the use of NPnEO surfactants in household laundry detergents. In all countries, the higher values were measured in rivers impacted by municipal and industrial wastewaters. The objective of the first part of this study was to investigate the occurrence of BT and TT in municipal wastewaters and to evaluate their behaviour in mechanical-biological wastewater treatment. In the second part of this project aimed at determining residual concentrations and mass flows of BT, TT, NP, OP and BPA in the Glatt River in Switzerland. The BT and TT concentrations reported in this article amend and substantially extend the data which were already earlier reported in an abstract publication (Schaffner and Giger 2004). The investigation on the phenolic compounds NP, OP and BPA is part of a comprehensive program dealing with the occurrence and the environmental behaviour of estrogenic substances in the aquatic environment of Switzerland. Previous studies have described the occurrence and behaviour of various organic micropollutants in the Glatt River, e.g. alkylphenolic compounds (Ahel et al. 1994b, 2000) and antibacterial agents (Golet et al. 2002, McArdell et al. 2003). In this report the data for NP in Glatt River are remeasured almost twenty years after the legal ban on the usage of NPnEO surfactants in laundry detergents was issued in Switzerland. The levels of the examined compounds are compared to the analogous concentrations reported for other rivers in other parts of the world.

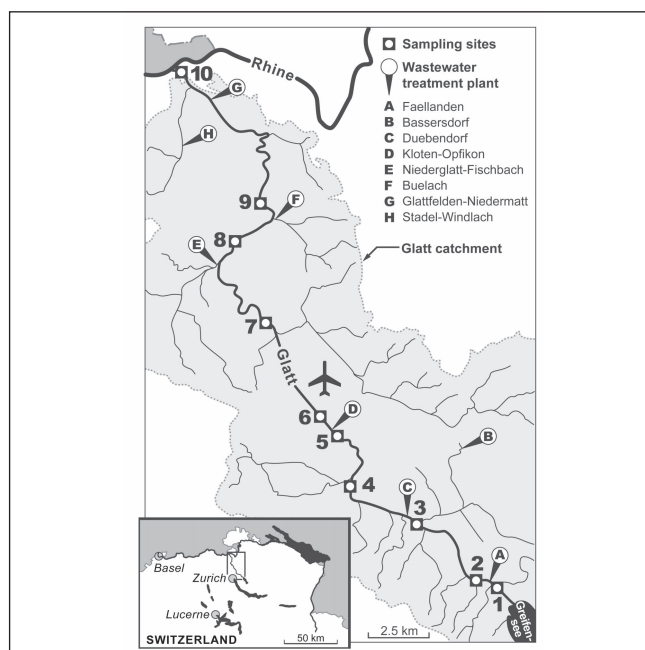
## 1 Experimental

### 1.1 Study area

The Glatt Valley is a densely populated region of 260 km<sup>2</sup> with 240,000 inhabitants in the northeastern part of Switzerland. The Glatt River catchment includes a northern part of the city of Zurich. The Glatt River has its origin as the outflow of Greifensee, has a total length of 36 km and is a tributary to the Rhine River. Water flows ranged from 1.7 to 10.9 m<sup>3</sup>/sec, the lower values were measured in August 2004. Ten municipal wastewater treatment plants (WWTPs) based on aerated sludge treatment discharge their final effluents into the Glatt River (A–H in Fig. 2) or its tributaries. Water flow data were supplied by the Cantonal Office for Waste, Water, Energy and Air of the Canton Zurich and the Swiss National Hydrological and Geographical Survey.

**Table 1:** Published occurrences of NP, OP and BPA in rivers

| River   | Sampling period   | NP (ng/L)   | OP (ng/L)                    | BPA (ng/L)                 | References   |
|---|---|---|------------------------------|----------------------------|--|
| <i>Switzerland</i><br>Glatt River   | 1983–1986<br>1997–1998  | 300–45,000<br><30–480   |                              |                            | Ahel et al. 1994b<br>Ahel et al. 2000  |
| <i>Germany</i><br>Elbe<br>Elbe and tributaries<br>Danube, Nau, Blau<br><br>Oder, Main, Nidda, Rhine | 1997<br>1998<br>2000<br>2000–2002<br>2000–2001<br>2000–2001<br>2000–2001<br>2000–2001 | 7.9–52<br>13–87<br>67–485<br>363–1,220<br>140–865<br><25–308<br>546–588 | 0.4–1.3<br><0.5–5<br>0.4–270 | 0.5–410<br>9–776<br><1–114 | Fromme et al. 2002<br>Heemken et al. 2001<br>Stachel et al. 2003<br>Bolz et al. 2001<br>Fries and Puettmann 2003<br>dito |
| <i>Austria</i>  | 2001  | nd–890  | nd–41                        | nd–600                     | ARCEM 2003   |
| <i>Belgium</i>  | 1999  | <LOQ  | <LOQ                         |                            | Ghijsen et al. 2000  |
| <i>The Netherlands</i>  | 1999–2002   | <50–6,300   | <nd–600                      | <8.8–1,000                 | Vethaak et al. 2002  |
| <i>Italy</i>  | 2002–2003   | <100–1,600  |                              |                            | Vitali et al. 2004   |
| <i>United Kingdom</i><br>Rivers in East and West Sussex   |   | <0.8  | <2.6–25                      | <5.3–13                    | Liu et al. 2004  |
| <i>Spain</i><br>Llobregat, Cardener, Anoia,<br>Riera de Rubi  | 2001  | <150–37,300   | <90–21,900                   | <90–2,970                  | Céspedes et al. 2005   |
| <i>Portugal</i>   | 2001/2  | nd–25,530   | nd–30,230                    | nd–5,030                   | Quiros et al. 2005   |
| <i>USA</i><br>Trenton Channel, Detroit River<br>Mississippi   | 1997<br>2003  | 269–1,190   | nd–81                        | 6–113                      | Snyder et al. 1999<br>Boyd et al. 2004   |
| <i>Canada</i><br>Upper St. Lawrence<br>St. Lawrence   | 1994–1995<br>1999   | <10–920<br><1   | 5–84<br><1–48                |                            | Bennie et al. 1997<br>Sabik et al. 2003  |
| <i>Japan</i><br>Tamagawa<br>Sumidagawa<br><br>Tama  | 1997<br>1997<br>1998–1999<br>1999–2003  | 80–1,080<br>50–170<br>110–3,080   | 10–180<br>10–70<br>10–90     | nd–230                     | Isobe et al. 2001<br>dito<br>Tsuda et al. 2000<br>Suzuki et al. 2004   |
| <i>Korea</i><br>Han River   | 2001  | 23.2–188  |                              |                            | Li et al. 2004   |
| <i>China</i><br>Haihe River   | 2003  | 106–296   | 18–20.2                      | 19.1–106                   | Jin et al. 2004  |

**Fig. 2:** Map of the Glatt Valley catchment indicating the locations of the municipal WWTPs A–H and the sampling sites 1–10 in the Glatt River

## 1.2 Sample collection and storage

Wastewater effluents were collected as 24-h flow proportional composite samples. During three sampling campaigns in June, August and October 2004 grab samples were taken at 10 sites along the Glatt River from the outflow of the Greifensee down to its mouth where it enters the Rhine River (sites 1–10 in Fig. 2).

Each sample was a mixture of grab samples collected from three sites across the river. The samples for NP, OP and BPA analysis were preserved with methylene chloride (1 ml/L) and stored at 4°C. The samples for BT and TT analysis were directly stored at 4°C.

## 1.3 Reagents and materials

BPA, fully deuterated BPA (BPA-d16), 4-*tert*-octylphenol (OP), 1H-benzotriazole (BT) and 5-methyl-1H-benzotriazole (tolyltriazole, 5-TT) were obtained from Aldrich; technical 4-nonylphenol (NP) and 4-*n*-nonylphenol (4nNP) were purchased from Riedel de Haen; 5,6-dimethyl-1H-benzotriazole monohydrate (5,6-dimethyl-BT) from Fluka. Stock solutions and standards were prepared in methanol except for 4nNP,

which was prepared in ethylacetate. The silylation derivatizing agents N-methyl-N-(trimethylsilyl)-trifluoroacetamide (MSTFA) and Sylon BTZ were obtained from Aldrich and Supelco, respectively. BondElute-PPL and OASIS HLB cartridges for SPE were purchased from Varian and Waters, respectively.

#### 1.4 Enrichment

**Enrichment of BT and TT.** Water samples (25 mL for wastewater, 100 mL for river water) were filtered through glass fibre filters (Whatman, GF/F 47mm), the filtrates were acidified to pH 2.5–3.0 and spiked with 50 ng of 5,6-dimethyl-1H-benzotriazole as surrogate standard. BT and TT were enriched from water by SPE through OASIS HLB cartridges (Waters, 60 mg, 3 mL). Solid-phase extraction was performed using a 12-port vacuum extraction manifold. The cartridges were sequentially conditioned with 2 x 3 mL of methanol and 2 x 3 mL of Milli-Q water by applying a slight vacuum. Water samples were percolated through the cartridges at a flow rate of 5 mL/min. The cartridges were dried under vacuum for 10 min and the analytes were eluted with 1.5 mL of dichloromethane containing 3% methanol. The eluates were evaporated to dryness under a gentle stream of nitrogen. Dry residues were redissolved in 0.5–1 mL of the LC mobile phase (methanol : water 7:3 with 0.4% formic acid).

**Enrichment of OP, NP and BPA.** Water samples were filtered through glass fibre filters (Whatman, GF/F 47 mm), the filtrates were adjusted to pH  $7.0 \pm 0.1$  and spiked with 100 ng of 4nNP and 100 ng of BPA-d16, as surrogate standards before extraction. The target compounds were recovered from 1 L of water by SPE through BondElute-PPL cartridges (Varian, 200 mg, 3 mL). Solid phase extraction was performed using a 12-port vacuum extraction manifold. Cartridges were sequentially conditioned with 2 x 2 mL acetone and 2 x 2 mL Milli-Q water by applying a slight vacuum. Water samples were drawn through the cartridges at a flow rate of 10 mL/min. The cartridges were dried under a gentle stream of nitrogen and the analytes were eluted with 2 x 2 mL acetone. The eluates were concentrated to dryness under a gentle stream of nitrogen. The dry residues were derivatized by the addition of 100  $\mu$ L derivatization agent MSTFA with 2% of Sylon BTZ, at 80°C for 30 min.

#### 1.5 Separation, detection and quantitation

**Determination of BT and TT.** Underivatized extracts dissolved in the LC mobile phase were analyzed by LC-MS/MS for BT and TT. 5,6-Dimethyl-BT served as surrogate standard. An HP Series 1100 system (Agilent) coupled with a triple quadrupole mass spectrometer (API 4000, Applied Biosystems) equipped with a vacuum solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector and a column thermostat was used. Separation was accomplished with a 125 x 2.1 mm i.d. endcapped C8 column (Macherey-Nagel, Düren, Germany). Isocratic elution was used with a mixture of methanol/water/formic acid (70:30:0.4) as a mobile phase at a flow rate of 0.2 mL/min. Detection of the analytes was accomplished with electrospray ionization in positive mode and using multiple reaction

monitoring (MRM). The following main ions  $[M+H]^+$  and two or three fragment ions for MS determination were chosen: for BT from m/z 120 to 64.85 and 92.05, for TT from m/z 134 to 76.85 and 78.95 and for 5,6-dimethyl-BT from m/z 148 to 77.05, 90.95 and 92.85. Due to the highly specific detection, only a partial chromatographic separation was necessary. Thus, short analysis times of only 5 min could be applied. Currently available LC separation performance did not achieve the separation of the 4- and 5-methyl-1H-benzotriazole isomers. As a consequence, the results are reported as the sum of the two isomers, noted by the common name tolyltriazole (TT). Quantification of BT and TT was carried out by calculating the relative response factors based on the area of 5,6-dimethyl-BT. Six calibration standard solutions (10 to 500 ng absolute) were used to produce a calibration curve for each compound relative to the internal standard. Recoveries were  $99 \pm 8\%$  for BT and  $97 \pm 10\%$  for TT. Limits of detection calculated as 3 times the standard deviation of low level standard were 8 ng/L for BT and 3 ng/L for TT. Limits of quantitation (10 times the standard deviation) were 30 and 10 ng/L for BT and TT, respectively.

**Determination of OP, NP and BPA.** The silylated derivatives of the analytes were subject to GC-MS analysis by using a gas chromatograph (Fisons 8000) equipped with an auto sampler and directly coupled to a mass spectrometer (Fisons MD 800). A DB-5 capillary column (30 m length, 0.32 mm id, 0.25  $\mu$ m film thickness, Agilent) was employed. Helium carrier gas was maintained at a constant flow rate of 1.2 mL/min. The GC column temperature was programmed from initial temperature 60°C for 1.5 min, raised to 180°C at 20°C/min, raised to 250°C at 5°C/min and finally to 290°C at 20°C/min, with the final temperature held for 5 min. Sample injection (2  $\mu$ L) was in splitless mode and the injector temperature was 220°C. The MS conditions were as follows: electron ionization (EI) mode at ionization energy of 70 eV, emission current of 150  $\mu$ A, ion source temperature at 220°C and transfer line at 280°C. A selected ion monitoring method was employed after solvent delay of initial 10 min.

The silylated derivatives of OP, NP, 4nNP, BPA, and BPA-d16 were identified based on matching retention times in comparison to calibration standards and by the ratio of target and qualifier masses. Under the above described conditions 10 peaks were obtained for the derivatized NP, and one peak was recorded for each of OP, BPA, 4nNP and BPA-d16. The characteristic ions of the derivatized compounds were m/z: 207.2, 208.3 for OP, 179.1, 193.2, 207.1, 221.2 for NP; 179.1 and 180.2 for 4nNP; 357.2 and 358.3 for BPA, 368.3 and 369.3 for BPA-d16.

Five calibration standard solutions were used to calculate response factors for each compound relative to the internal standard. Quantification of OP and BPA was carried out by calculating the relative response factors based on the area of 4nNP and BPA-d16, respectively. NP was quantified comparing the integrated peak area of the summed selected ions with the peak area of 4nNP. For the quantification of NP the ion traces with the smallest interferences were used.

During the analytical procedure only glass or steel tools (350°C, 24 h) flushed with hexane, acetone and methanol were used. All solvents were of high analytical grade. Proce-



dural blanks were checked. The recoveries evaluated by replicate analyses of river water spiked with standard solutions ranged from 90 to 122%. The limits of detection, calculated as 3 times the standard deviation of the low level standard, were 12.7, 0.5 and 2.4 ng/L for NP, OP and BPA, respectively. The limits of quantitation, calculated as 10 times the standard deviation of the low level standard, were 40, 1.7 and 7 ng/L for NP, OP and BPA, respectively.

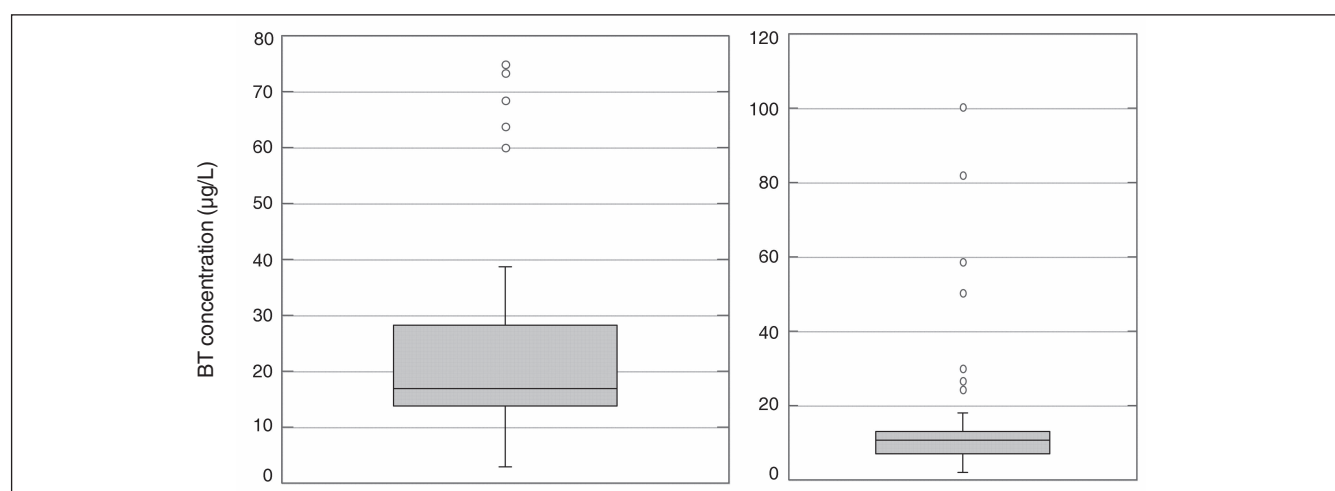
## 2 Results and Discussion

### 2.1 Concentrations in municipal wastewaters

BT and TT were found in the  $\mu\text{g/L}$  range in all samples of primary and secondary effluents from 24 municipal WWTPs in Switzerland. The BT concentrations were always by a factor of 10 to 100 higher than the corresponding TT values. Fig. 3 shows box plots for all BT concentrations meas-

ured in primary and secondary effluents. The median values for BT concentrations in primary and secondary effluents are 18 and 10  $\mu\text{g/L}$  respectively. It is evident that both concentration sets contain several outliers with two remarkably high BT concentrations of 100 and 83  $\mu\text{g/L}$  in the secondary effluents. It can be inferred, that the occurrence of BT in municipal wastewaters is caused by its application as an anticorrosive additive in dishwasher products. This conclusion could be corroborated by analyses of dishwasher detergent products and of raw municipal wastewaters in the town of Duebendorf (Ort 2006, Ort et al. 2006). It is currently not clear, how TT gets into municipal wastewaters, because most of its applications are not directly connected to municipal wastewaters.

The eliminations of BT and TT in WWTPs are relatively low as it is illustrated by the results from 10 WWTPs in the Glatt Valley catchment shown in Table 2 (for locations see



**Fig. 3:** BT concentrations in primary and secondary effluents (left and right graph, respectively) measured in 24 municipal WWTPs in the Glatt Valley catchment in Switzerland. The box plots indicate 25<sup>th</sup> and 75<sup>th</sup> percentiles, median and outlier concentrations. Number of analyzed samples: 33 primary effluents, 61 secondary effluents. The samples were collected from 2002 to 2005

**Table 2:** BT and TT concentrations in municipal wastewater and elimination rates in 10 WWTPs in Switzerland. Concentrations are average values of double determinations based on 24 h composite samples collected in May and June 2003. WWTPs A to H are discharging into the Glatt River as shown on the map of Fig. 2. The values for WWTP D are averages based on 7 consecutive 24 h composite samples collected from 18 to 24 November 2002 (see Fig. 4A). The eliminations for WWTP D were calculated based on the concentrations after the sand filter

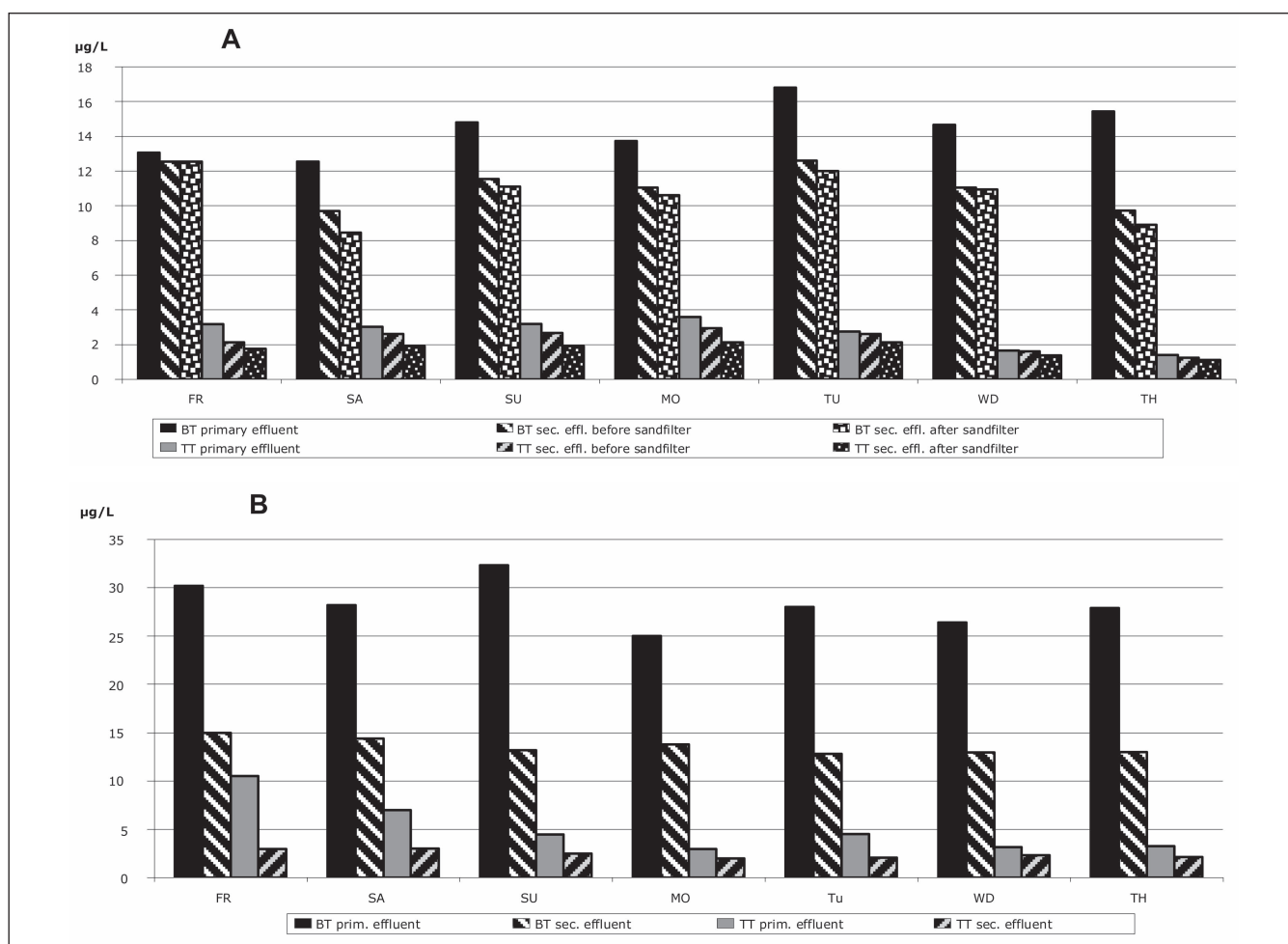
| Wastewater treatment plant |                | Concentrations ( $\mu\text{g/L}$ ) |           |               |               |           |               |
|----------------------------|----------------|------------------------------------|-----------|---------------|---------------|-----------|---------------|
|                            |                | Benzotriazole                      |           |               | Tolyltriazole |           |               |
|                            |                | effluent type                      |           |               | effluent type |           |               |
|                            |                | primary                            | secondary | elimination % | primary       | secondary | elimination % |
| A                          | Fällanden      | 22                                 | 12        | 45            | 4.0           | 1.8       | 55            |
| B                          | Bassersdorf    | 60                                 | 58        | 3             | 1.1           | 0.9       | 18            |
|                            |                | 75                                 | 30        | 60            | 1.1           | 0.8       | 27            |
|                            |                | 73                                 | 50        | 32            | 1.6           | 0.7       | 44            |
| C                          | Dübendorf      | 17                                 | 11        | 35            | 2.3           | 0.7       | 70            |
| D                          | Kloten-Opfikon | 14                                 | 11        | 23            | 2.7           | 1.8       | 33            |
| E                          | Niederglatt    | 64                                 | 82        | -28           | 3.2           | 2.3       | 28            |
|                            |                | 68                                 | 100       | -47           | 3.1           | 2.4       | 23            |
| F                          | Bülach         | 39                                 | 15        | 62            | 2.9           | 1.2       | 58            |
|                            |                | 27                                 | 13        | 52            | 2.5           | 1.2       | 52            |
| G                          | Glattfelden    | 15                                 | 13        | 13            | 0.2           | 0.1       | 50            |
| H                          | Stadel         | 14                                 | 11        | 21            | 2.3           | 0.6       | 74            |
| I                          | Mönchaltorf    | 13                                 | 11        | 15            | 5.6           | 3.8       | 25            |
| K                          | Uster          | 16                                 | 11        | 31            | 5.4           | 1.9       | 65            |

Fig. 2). The BT levels in primary effluents ranged from 13 to 39  $\mu\text{g/L}$ , whereas in the two WWTPs B and E substantially higher BT concentrations were observed (60–75  $\mu\text{g/L}$ ). The effluents of the WWTPs B and E caused the outlier values in Fig. 3. The higher BT inputs to these two WWTPs can currently not be explained. It is, however suspected that there could be some special inputs from small industries. Currently, no conclusive information is available on the input sources of the TT found in municipal wastewaters. The latter showed in the WWTPs of the Glatt Valley relatively narrow ranges: 1.1–5.6 and 0.1–3.8  $\mu\text{g/L}$  in primary and secondary wastewater effluents, respectively (see Table 2). In WWTP E the BT concentrations even increased from the primary to the secondary effluent. It is assumed that this effect can either be caused by an input variation or a formation during the treatment. For the latter there would be a need for a precursor chemical. WWTP B showed drastically different elimination rates for BT (3, 32 and 60%). Again an input variation could be invoked to explain this result. If the special WWTPs B and E are not taken into account, the elimination for TT were generally higher (23–74%) compared to the corresponding values for BT (13–62%). This difference could be caused by the slightly better biodegradability of the methylated benzotriazole (TT).

WWTP B gave again an exceptional result: TT was only eliminated by 18% in the same sampling campaign, in which the elimination rate for BT was only 3%.

A wastewater investigation in Berlin yielded results within the concentration ranges reported here. The concentrations were 11.9 and 9.6  $\mu\text{g/L}$  for BT in the influent and in the effluent of one WWTP (Weiss and Reemtsma 2005). The corresponding concentrations for the separated TT isomers in the influent were 2.5 and 2.2  $\mu\text{g/L}$  for 5-TT and 4-TT, respectively. The analogous values for the effluent were 2.0 and 2.1  $\mu\text{g/L}$ .

Fig. 4 shows the results of weekly profiles measured at the two WWTPs Kloten-Opfikon and Thun. In both places, no decreases could be observed over the weekends indicating an industrial input, which would be higher during the week days. The BT levels decreased in the biological treatment of the WWTP Kloten-Opfikon from 2 to 30%. The sand filter had a very little impact. In the WWTP Thun BT and TT show higher concentrations and higher eliminations. The higher input levels are attributed to the large number of automobile repair shops in city of Thun. Despite the relatively high elimination in the WWTP Thun, the residual concentrations are still in the range of the input levels in the other WWTPs.



**Fig. 4:** Weekly profiles of BT and TT concentrations in primary and secondary effluents at two municipal WWTPs in Switzerland. A: Kloten-Opfikon, Canton Zurich ; B: Thun, Canton Berne. 24 h composite samples for A and B were collected from November 18 to 24, 2002 and from March 21 to 27, 2003, respectively

## 2.2 Concentrations and mass flows in the Glatt River

The concentrations of BT, TT, NP, OP and BPA determined along Glatt River, Switzerland in June, August and October 2004 are displayed in Fig. 5 and Fig. 6. The BT concentrations in the Glatt River ranged from 636 to 3,690 ng/L. The TT concentrations were 3–6 times lower as for BT, ranging from 122 to 628 ng/L. The highest BT concentrations found at sites 8 and 9 (3,600 and 3,350 ng/L). An increasing trend along the longitudinal profile of the river was observed for BT and TT. The sharpest increase was in the June sample from sampling station 7 to 8. This could possibly be explained by the contribution of the WWTP Niederglatt which discharges its effluent after sampling site 7 and shows high residual BT concentrations (see Table 2). The concentrations of BT and TT found in this study are similar to the concentrations previously published for the Glatt River (1,000–5,500 ng/L for BT and 200–1,000 ng/L for TT), whereas lower concentrations were reported for the larger Rhine River below Basel (200–500 ng/L for BT and 50–200 ng/L for TT) (Schaffner and Giger 2004). There are very few data available in the literature on the presence of these compounds in ambient waters. Most of the published data emphasize the presence of these compounds in run-off from airports after anti-icing and de-icing activities and on water bodies, which are directly impacted by these fluids. Cancilla et al. (1998) published estimated concentrations in mg/L in subsurface water close to an airport: 126 for BT and 17 for 4-TT as well as 198 for total TT. High levels of BT have also been determined in a secondary airport runoff outfall (1.67 and 2.16 mg/L for 4- and 5-TT), whereas the concentrations in receiving streams were less than 0.08 mg/L (Cancilla et al. 2003). A small number of results of surface water and bank filtrate analy-

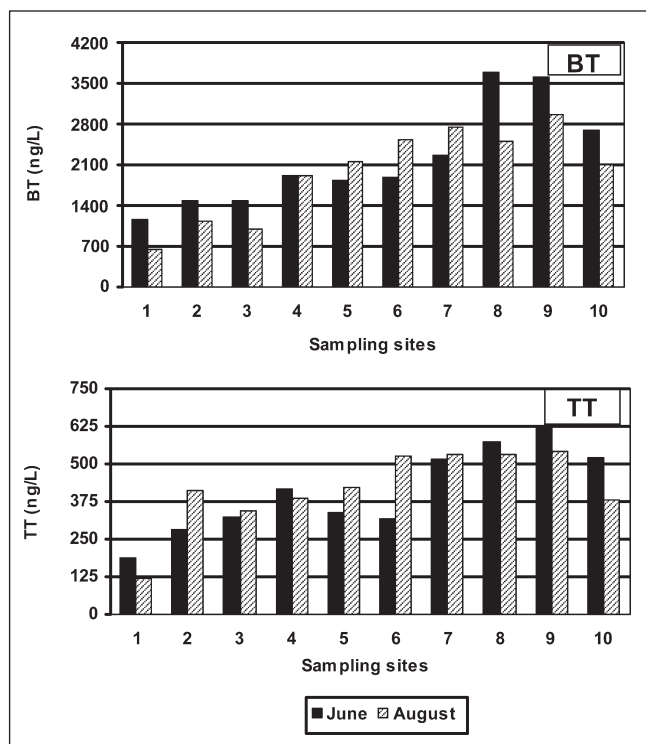


Fig. 5: BT and TT concentrations in a longitudinal profile of the Glatt River

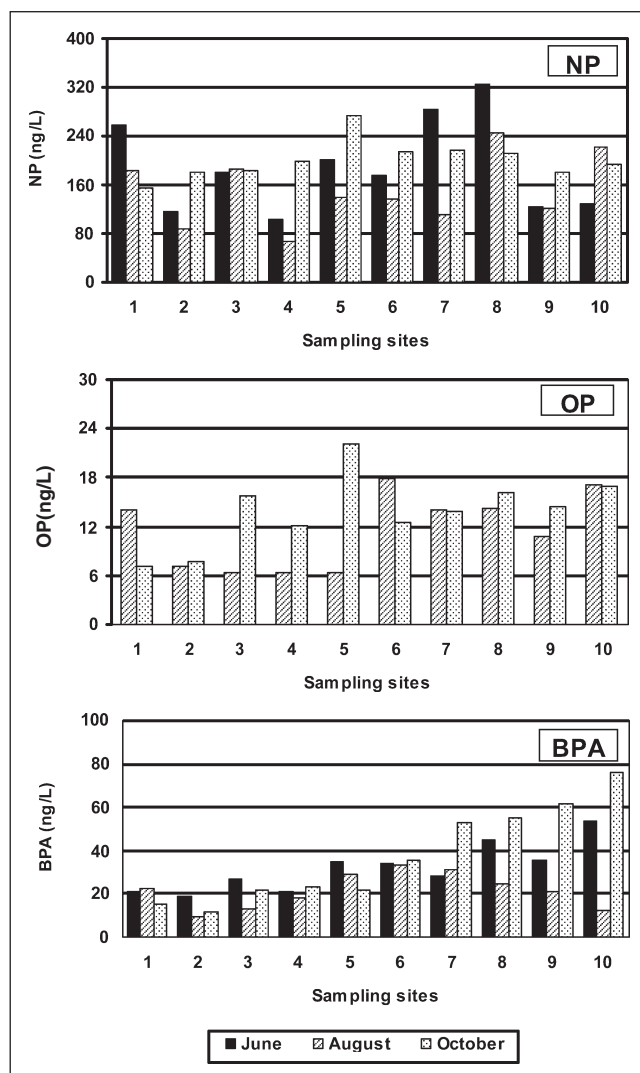
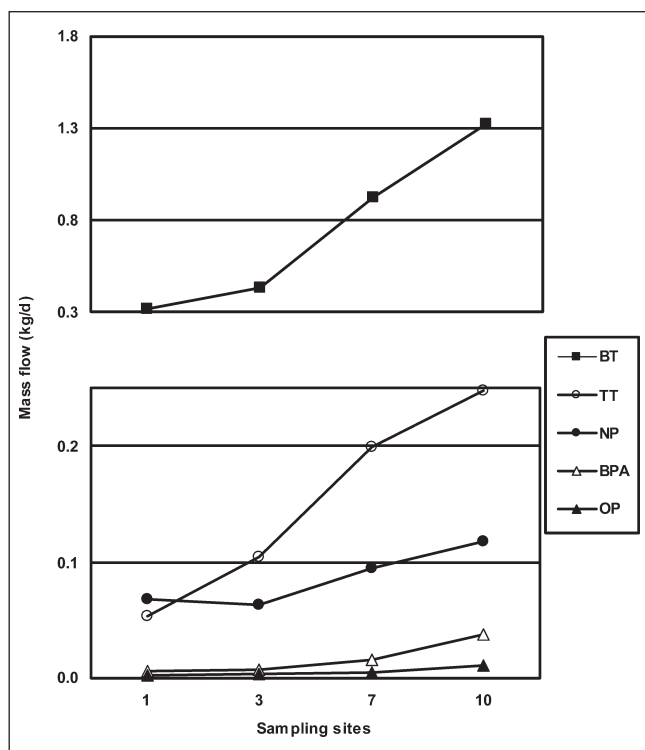


Fig. 6: NP, OP and BPA concentrations in a longitudinal profile of the Glatt River

ses from the Berlin area were recently published (Weiss and Reemtsma 2005). In Lake Tegel 0.9 µg/L BT and 0.2 µg/L TT were detected and in the corresponding bank filtrate 0.2 and 0.05 µg/L were measured for BT and 4-TT. In 2 samples from the Landwehr Canal the average concentrations in µg/L were 0.9 for BT, 0.2 for 4-TT and 0.1 for 5-TT.

In the Glatt River NP was by far the most abundant among the examined phenolic compounds concentrations ranging from 68–326 ng/L. Higher NP levels were observed at sites 8, 1, 7, 5 and 3. The NP concentrations in the Glatt River are within the range reported for surface waters that are weakly impacted by municipal or industrial wastewaters (see Table 1).

A significant reduction of NP concentrations in the Glatt River compared to those reported for the same river (300–4,500 ng/L) during the time period 1983–1986 was observed (Ahel et al. 1994b). This reduction is due to the restriction in use of the corresponding compounds in Switzerland through corrective actions including the ban of NPnEOs from house-



**Fig. 7:** Average mass flows of BT, TT, NP, OP and BPA in a longitudinal profile of the Glatt River

hold products and potentially a reduction of their industrial use. These actions led to the reduction of NPnEOs and their metabolites in the effluents from WWTPs, which are the main sources for the residual amounts appearing in surface waters. The concentrations of NP in secondary effluents from wastewater treatment plants along Glatt valley have been significantly reduced during last twenty years, i.e. from 22 to 0.4  $\mu\text{g/L}$  in effluents from WWTP C at Dübendorf or from 35.2 to <0.3  $\mu\text{g/L}$  in effluents from WWTP D at Kloten-Opfikon (Ahel et al. 1994a, Ahel et al. 2000, Wettstein 2004).

The OP concentrations in Glatt River ranged from 6–22 ng/L and were one order of magnitude lower than NP. The concentrations of OP in the Glatt River are within the range determined in other surface waters (see Table 1), although a broader range is reported in the literature. The occurrence of NP and OP did not follow any significant trend along the river, although it is assumed that wastewater effluents are the major inputs. It is possible that biodegradation might affect their occurrence along the river. Some lower concentrations of NP and OP were found during August, but no consistent seasonal trend or temperature dependence was found. Lower concentrations of NP in surface waters during summer were reported by Ahel et al. (1994b) and were attributed to the lower input and/or to the better elimination of these compounds during warmer months. However, other investigators published higher NP concentrations in summer due to the higher degradation rate of APEOs under higher temperatures (Li et al. 2004, Isobe et al. 2001).

The BPA concentrations in Glatt River ranged from 9 to 76 ng/L (see Fig. 6). Higher concentrations of BPA were observed in the lower part of the river (sites 6 to 10). The

spatial distribution of BPA was different from the distribution of NP and OP. Particularly for the June and even more for the October values an increasing trend of the BPA concentrations along the Glatt River was found. The August values, however, did not show this trend, which might be caused by the higher water temperatures in August accelerating biodegradation in the river (see Table 1).

Mass flows for BT, TT, NP, OP and BPA along the Glatt River were calculated on the basis of their concentrations and the water flows at the sites 1, 3, 7 and 10, for which the latter were available (Fig. 7). The mass flows in g/d were 93–1,870 for BT, 18–360 for TT, 24–183 for NP, 0.9–16 for OP and 2–72 for BPA. Lower mass flows were found in August caused by relatively low concentrations as well as by the lower water flows which amounted to 1.7–4.1  $\text{m}^3/\text{s}$  in August compared to 4.2–10.9  $\text{m}^3/\text{s}$  in June and October. Generally, the mass flows for all target contaminants tended to increase along the river longitudinal profile indicating additional incremental inputs and no rapid elimination. For a reliable assessment of the elimination behaviour of these pollutants in the Glatt River, it would, however, be necessary to perform a more detailed study including all WWTP inputs and aiming at mass flow analyses.

### 3 Conclusions and Perspectives

The anticorrosive agents BT and TT occur in all municipal wastewater effluents and are only partly removed in mechanical-biological wastewater treatment because of their high polarity, i.e. high solubility in water, and their resistance to biodegradation. Thus, residual amounts of BT and TT are widely distributed in the receiving ambient waters. In particular, BT is – after EDTA – the second most abundant individual contaminant in many natural waters. BT can be tracked back to its use as an anticorrosive agent in dishwasher detergents. However, the question remains unanswered, how TT is entering municipal wastewaters. Regarding BT and TT it will be interesting to investigate, whether discharges in the winter season from the international airport of Zurich have an impact on the concentrations and loads in the Glatt River. The airport is located close to the Glatt River (see Fig. 2). At the airport antifreezing and de-icing liquids are applied, which contain BT as an additive for the inhibition of corrosion. Additional questions of concern are, how BT and TT behave during bank filtration and how they are affected by the various procedures of drinking water treatment plants using lake water as a water resource.

Concentrations and mass flows in wastewater effluents and in the Glatt River almost always followed the same sequence of abundance:  $\text{BT} > \text{NP} > \text{TT} > \text{BPA} > \text{OP}$ . The concentration ranges observed in the Glatt River are considered to be within the corresponding ranges reported for weakly contaminated surface waters. Based on a comparison to earlier NP concentrations and mass flows it can be concluded that the risk management efforts had a highly significant impact. The mitigation measures included a partial legal ban and voluntary restrictions of the use of nonylphenol polyethoxylate surfactants but also the performance improvement of the WWTPs mainly by enlarging the overloaded plants. In addition to the studies reported in this article, there should be



an analogous investigation scrutinizing the occurrence and behaviour of nonylphenoxy acetic acid, which is notoriously the most abundant metabolite of nonylphenol polyethoxylates in biologically treated sewage effluents.

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